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## PATENT ABSTRACTS OF JAPAN

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### (54) THERMOPLASTIC POLYESTER RESIN COMPOSITION

#### (57)Abstract:

PROBLEM TO BE SOLVED: To obtain a thermoplastic polyester resin composition having not only mechanical characteristics and durability but also sufficiently excellent moldability.

SOLUTION: This thermoplastic polyester resin composition is obtained by compounding 100 pts.wt. of a thermoplastic polyester resin (A) with 0.1-10 pts.wt. of a carboxylic acid reactive group-containing polymer (B-1) and/or a compound (B-2) containing plural oxazoline groups in the molecule and 0.01-5 pts.wt. of a carboxylic acid anhydride (C). Another thermoplastic polyester resin composition is obtained by melting and kneading 100 pts.wt. of the component A with 0.1-10 pts.wt. of the component (B-1) and/or the component (B-2) and 0.01-5 pts.wt. of the component C. This method for producing thermoplastic polyester resin molding product is a method for producing a molding product comprising the thermoplastic polyester resin as a material and is obtained by molding the thermoplastic polyester resin composition.

### LEGAL STATUS

[Date of request for examination]

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CLAIMS

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[Claim(s)]

[Claim 1] The thermoplastic polyester resin constituent characterized by coming to blend the compound (B-2) which has two or more oxazoline radicals, and the carboxylic anhydride (C) of 0.01 - 5 weight section into the polymer (B-1) which has the carboxylic-acid reactivity radical of 0.1 - 10 weight section, and/or a molecule to the thermoplastic polyester (resin A) 100 weight section in the thermoplastic polyester resin constituent which uses thermoplastic polyester resin as an indispensable component.

[Claim 2] thermoplastic polyester -- resin -- (-- A --) -- 100 -- weight -- the section -- a carboxylic acid -- reactivity -- a radical -- having -- a polymer (B-1) -- and/or -- a molecule -- inside -- plurality -- oxazoline -- a radical -- having -- a compound (B-2) -- 0.1 - ten -- weight -- the section -- and -- a carboxylic anhydride -- (-- C --) -- 0.01 - five -- weight -- the section -- melting -- kneading -- carrying out -- becoming -- thermoplastic polyester -- resin -- a constituent .

[Claim 3] The thermoplastic polyester resin constituent according to claim 1 or 2 whose carboxylic-acid reactivity radicals in said polymer (B-1) are an oxazoline radical and/or an epoxy group.

[Claim 4] A thermoplastic polyester resin constituent given in either to claims 1-3 which has the number average molecular weight of said polymer (B-1) in the range of 1000-20000. --

[Claim 5] The manufacture approach of the thermoplastic polyester resin Plastic solid which is the approach of manufacturing a Plastic solid made from thermoplastic polyester resin, and is characterized by fabricating using the thermoplastic polyester resin constituent of a publication to either to claims 1-4.

[Claim 6] The manufacture approach of a thermoplastic polyester resin Plastic solid according to claim 5 that said shaping is at least one sort chosen from extrusion molding, injection molding, blow molding, foaming, and spinning shaping.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a thermoplastic polyester resin constituent and its operation. It is related with the thermoplastic polyester resin constituent excellent in the moldability, and its operation in more detail.

[0002]

[Description of the Prior Art] Although the polyalkylene terephthalate represented with thermoplastic polyester resin especially polyethylene terephthalate (PET), and polybutylene terephthalate is widely used also as a material of industrial use fiber, a film, and other Plastic solids since it has the property which was excellent in many, the more excellent mechanical property, thermal resistance, hydrolysis-proof nature, and a moldability are demanded. In order to present blow molding and extrusion molding especially, generally, melt viscosity of polyester resin is too low, drawdown is intense and it is most difficult to obtain the mold goods of a desired configuration. Moreover, since melting was repeated between recovery actuation when recycle use of the disposal PET is carried out, intrinsic viscosity (IV) fell, it was not suitable for spinning shaping any longer, and fiber with sufficient reinforcement and sufficient ductility was not able to be obtained. In order to improve these, it is effective to raise a degree of polymerization and to decrease the end carboxyl group in polyester, and there is an approach using the chain elongation agent which can react with the end group of polyester resin and can extend a polymer chain as an approach of denaturalizing polyester for such the purpose. For example, the approach (JP,55-161823,A) using a bis-oxazoline compound, the approach (JP,47-13860,B, JP,2-276820,A, JP,5-506056,A) using a polyfunctional compound, etc. are examined.

[0003] However, by these approaches, although a mechanical property, thermal resistance, and hydrolysis-proof nature can be given to polyester resin to some extent, it is one side and sufficient engine performance cannot be given about a moldability. For example, by the approach (JP,55-161823,A) using the aforementioned bis-oxazoline compound, it cannot say that a mechanical property and endurance are also enough, and they cannot give sufficient melt viscosity for it to be suitable for the various fabricating methods further, and IV. moreover, by the approach (JP,47-13860,B, JP,2-276820,A, JP,5-506056,A) using the aforementioned polyfunctional compound When too sufficient melt viscosity and IV cannot be given when a polyfunctional epoxy compound, polyfunctional isocyanate, etc. are used, but it applies to extrusion molding, injection molding, and blow molding When there was a fault that detailed foam uniform since resin viscosity is low is not obtained when there is a fault that resin will carry out drawdown and it applies to foaming, since molecular weight is not enough and it applied to spinning shaping, there was a fault that the thread breakage in spinning happened. Moreover, if the addition of those compounds is increased in order to raise melt viscosity, a constituent gels and it is known that a moldability will worsen remarkably. Furthermore, these polyfunctional compound vaporized in the forming cycle, and there were problems, such as spoiling the appearance of a lifting and mold goods, about metal mold contamination.

[0004]

[Problem(s) to be Solved by the Invention] Therefore, the technical problem which this invention tends to solve is offering the thermoplastic polyester resin constituent which it not only excels in a mechanical property and endurance, but has the moldability which was fully excellent.

[0005]

[Means for Solving the Problem] this invention person inquired wholeheartedly that the above-mentioned technical problem should be solved. Consequently, the constituent obtained by blending a carboxylic anhydride and the compound which has a specific radical in a further specific reactant radical content polymer and/or a molecule at thermoplastic polyester resin could solve the above-mentioned technical problem, and found out that it was applicable suitable for the various shaping approaches. This invention was carried out in this way, and was completed.

[0006] That is, it is characterized by the thermoplastic polyester resin constituent concerning this invention coming to blend the compound (B-2) which has two or more oxazoline radicals, and the carboxylic anhydride (C) of 0.01 - 5 weight section into the polymer (B-1) which has the carboxylic-acid reactivity radical of 0.1 - 10 weight section, and/or a molecule to the thermoplastic polyester (resin A) 100 weight section in the thermoplastic polyester resin constituent which uses thermoplastic polyester resin as an indispensable component.

[0007] moreover -- this invention -- starting -- being another -- thermoplastic polyester -- resin -- a constituent -- thermoplastic polyester -- resin -- (-- A --) -- 100 -- weight -- the section -- a carboxylic acid -- reactivity -- a radical -- having -- a polymer (B-1) -- and/or -- a molecule -- inside -- plurality -- oxazoline -- a radical -- having -- a compound (B-2) -- 0.1 - ten -- weight -- the section -- and -- a carboxylic anhydride -- (-- C --) -- 0.01 - five -- weight -- the section -- melting kneading -- carrying out -- becoming .

[0008] Moreover, the manufacture approach of the thermoplastic polyester resin Plastic solid concerning this invention is an approach of manufacturing a Plastic solid made from thermoplastic polyester resin, and is characterized by fabricating using the thermoplastic polyester resin constituent of this invention.

[0009]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail.

(Constituent) It is characterized by the thermoplastic polyester resin constituent concerning this invention coming to blend the compound (B-2) which has two or more oxazoline radicals, and the carboxylic anhydride (C) of 0.01 - 5 weight section into the polymer (B-1) which has the carboxylic-acid reactivity radical of 0.1 - 10 weight section, and/or a molecule to the thermoplastic polyester (resin A) 100 weight section in the thermoplastic polyester resin constituent which uses thermoplastic polyester resin as an indispensable component.

[0010] moreover -- this invention -- starting -- being another -- thermoplastic polyester -- resin -- a constituent -- thermoplastic polyester -- resin -- (-- A --) -- 100 -- weight -- the section -- a carboxylic acid -- reactivity -- a radical -- having -- a polymer (B-1) -- and/or -- a molecule -- inside -- plurality -- oxazoline -- a radical -- having -- a compound (B-2) -- 0.1 - ten -- weight -- the section -- and -- a carboxylic anhydride -- (-- C --) -- 0.01 - five -- weight -- the section -- melting kneading -- carrying out -- becoming .

[0011] Hereafter, the resin constituent concerning these this inventions is explained first. As thermoplastic polyester resin (A) used in this invention, the polyester which consists of acid components, such as a terephthalic acid, isophthalic acid, naphthalene dicarboxylic acid; diphenyl ether dicarboxylic acid, a succinic acid, an adipic acid, a sebacic acid, cyclohexane dicarboxylic acid, and a hydroxybenzoic acid, and glycol components, such as ethylene glycol, a trimethylene glycol, tetramethylene glycol, hexamethylene glycol, and cyclohexane dimethanol, is mentioned. Moreover, components of three or more organic functions other than the 2 above-mentioned organic-functions components, such as trimellitic acid and pentaerythritol, may be copolymerized. Moreover, the copoly ester which combined the polyether ester which consists of residue of aromatic series ether dicarboxylic acid, such as poly lactone [ , such as polyester guided from oxy acid and those residue, such as a p-oxy-benzoic acid, and poly PIPARO lactone, ], 1, and 2-bis(4 and 4-dicarboxy methylphenoxy) ethane, and the above-mentioned glycol component, the dicarboxylic acid described further above, oxy acid, and

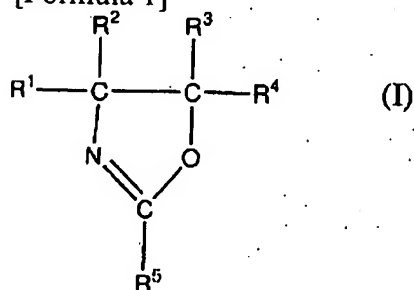
glycols can be mentioned. Furthermore, the block copolymerized polyester to which coupling of two or more sorts of low-molecular-weight polyester was carried out using 2 functionality chain elongation agent can be mentioned.

[0012] Polyethylene terephthalate and polybutylene terephthalate are desirable in these polyester. Moreover, it was obtained from fabrication operation or the abandonment after use, for example, the abandonment PET of the gestalt of a film, a sheet, fiber, bottle mold goods, etc. can also be used. The polymer (B-1) which has the carboxylic-acid reactivity radical which can be used in this invention means a carboxylic acid and the polymer which has the functional group which can react. Here, although for example, an oxazoline radical and an epoxy group are mentioned, a carboxylic acid and the functional group which can react are oxazoline radicals preferably, in order to fully demonstrate the effectiveness of this invention. As for said functional group which it has in a polymer (B-1), at least one sort may be two or more sorts.

[0013] When a polymer (B-1) has an oxazoline radical, it is a general formula (I).

[0014]

[Formula 1]



[0015] the inside of a formula, R1, R2, R3, and R4 -- respectively -- independent -- hydrogen and a halogen -- alkyl, an aralkyl, phenyl, or permutation phenyl -- it is -- R5 It is an un-annular organic radical with an addition polymerization nature unsaturated bond. They are the addition polymerization nature oxazoline compound (b-1) expressed and the polymer which has two or more oxazoline radicals as a side chain which comes to carry out the polymerization of at least one sort of other monomers (b-2) if needed.

[0016] As an example of said addition polymerization nature oxazoline compound (b-1) For example, 2-vinyl-2-oxazoline, 5-methyl-2-vinyl-2-oxazoline, 4 and 4-dimethyl-2-vinyl-2-oxazoline, 4, and 4-dimethyl-2-vinyl -5, 5-dihydro-4H-1, 3-oxazine, Although vinyl oxazoline, such as 4, 4, 6-trimethyl-2-vinyl -5, 6-dihydro-4H-1, 3-oxazine, 2-isopropenyl-2-oxazoline, 4, and 4-dimethyl-2-isopropenyl-2-oxazoline, is mentioned It is not limited to especially these. Also in the monomer which has these oxazoline radical, since [ for acquisition / that 2-isopropenyl-2-oxazoline is easy and ] reactivity is good, it is desirable.

[0017] Although especially the amount of the addition polymerization nature oxazoline compound (b-1) used is not limited, it is desirable among an oxazoline radical content polymer that it is [ 0.5 % of the weight or more ] less than 50 % of the weight. Less than 0.5% of the weight of the amount of a moldability and the heat-resistant improvement effectiveness is inadequate, and even if it uses it 50% of the weight or more, effectiveness does not change but is economically disadvantageous.

[0018] If a monomer (b-2) besides the above does not react with an oxazoline radical but are addition polymerization nature oxazoline (b-1) and a copolymerizable monomer There is especially no limit. For example, a methyl acrylate (meta), butyl acrylate (meta), (Meta) acrylic ester [ , such as 2-ethylhexyl acrylate, ] (meta); (meta) -- unsaturated nitrile [ , such as acrylonitrile, ]; (meta) -- acrylamide -- Partial saturation amides, such as N-methylol(metha)acrylamide; Vinyl acetate, Vinyl ester, such as propionic-acid vinyl; The methyl vinyl ether, Vinyl ether, such as ethyl vinyl ether; Alpha olefin; vinyl chlorides, such as ethylene and a propylene, Halogen-containing [ , such as vinylidene-chloride, vinyl, etc. fluoride, ] alpha and beta-partial saturation monomers; alpha, such as styrene and alpha methyl styrene, and beta-partial saturation aromatic series monomers are mentioned, and one sort or two sorts or more of

such mixture can be used.

[0019] When a polymer (B-1) has an epoxy group, they are the monomer (b-3) which has an epoxy group, and the polymer which has two or more epoxy groups as a side chain which comes to carry out the polymerization of the same monomers (b-2) of other as at least one sort of above-mentioned if needed. As an example of a monomer (b-3) of having said epoxy group, although glycidylethers of partial saturation organic acids, such as metaglycidyl acrylate, glycidyl methacrylate, glycidyl ethacrylate, and itaconic-acid glycidyl, such as glycidyl ester; allyl glycidyl ether, etc. are mentioned, it is not limited especially, for example. Also in these, metaglycidyl acrylate and glycidyl methacrylate are desirable.

[0020] A polymer (B-1) can manufacture conventionally for example, an addition polymerization nature oxazoline compound (b-1) and/or an epoxy group content monomer (b-3), and the monomer component that consists of at least one sort of other monomers (b-2) if needed by the well-known polymerization method, for example, a solution polymerization method, the suspension-polymerization method, the emulsion-polymerization method, a bulk polymerization method, etc. In measurement of GPC (gel permeation chromatography), the number average molecular weight of the polymer (B-1) which has the carboxylic-acid reactivity radical used in this invention has the desirable range of 1000-20000, and especially its range of 1500-10000 is desirable. Since the molecular weight of the constituent of this invention with which number average molecular weight is obtained less than by 1000 is not enough, even if there is an inclination for a moldability to worsen, and the heat-resistant improvement effectiveness moreover also tends to decrease and it exceeds 20000, it is in the inclination for the moldability of the constituent of this invention obtained to be inferior.

[0021] Although especially the supply gestalt of a polymer (B-1) is not restricted, the field of handling to a solid or an organic solvent solution is desirable, and especially a solid is desirable. With the compound (B-2) which can be used in this invention and which has two or more oxazoline radicals in a molecule For example, 1, 3-phenylene screw (2-oxazoline), 1, 4-phenylene screw (2-oxazoline), 2 and 2-screw (2-oxazoline), 2, and 2-screw (4-methyl-2-oxazoline), 2 and 2-screw (4 and 4-dimethyl-2-oxazoline), 2, and 2-screw (4-ethyl-2-oxazoline), 2 and 2-screw (4 and 4-diethyl-2-oxazoline), 2, and 2-screw (4-propyl-2-oxazoline), 2 and 2-screw (4-butyl-2-oxazoline), 2, and 2-screw (4-hexyl-2-oxazoline), 2 and 2-screw (4-phenyl-2-oxazoline), 2, and 2-screw (4-cyclohexyl-2-oxazoline), 2 and 2-screw (4-benzyl-2-oxazoline), 2, and 2-ethylene screw (2-oxazoline), 2 and 2-tetra-methylenebis (2-oxazoline), 2, and 2-hexa methylenebis (2-oxazoline), 2 and 2-octamethylene screw (2-oxazoline), 2, and 2-ethylene screw (4-ethyl-2-oxazoline), Although bis-oxazoline compounds, such as 2 and 2-tetra-ethylene screw (4-ethyl-2-oxazoline), 2, and 2-cyclo hexylene screw (4-ethyl-2-oxazoline), are mentioned, 1 and 3-phenylene screw (2-oxazoline) is mentioned preferably.

[0022] The carboxylic anhydride (C) used in this invention has two anhydrides of for example, aromatic series tetracarboxylic acid, especially pyromellitic acid 2 most desirable anhydride. As other useful carboxylic anhydrides, for example 3, 3', 4, 4'-diphenyl tetracarboxylic acid, Tetracarboxylic acid, 3, 3', 4, 4'-benzophenone tetracarboxylic acid, (Perylene - 3, 4, 9, 10) A 2 and 2-bis(3, 4-dicarboxy phenyl) propane, the bis(3, 4-dicarboxy phenyl) ether, Anhydrides, such as a bis(3, 4-dicarboxy phenyl) sulfone, 1, 2 and 3, 4-cyclobutane tetracarboxylic acid and 2, 3 and 4, a 5-tetra-carboxy hydronalium furan, a phthalic acid, and a maleic acid, are mentioned.

[0023] A carboxylic anhydride (C) may be a polymer, for example, may be the copolymer of styrene and a maleic anhydride. One gestalt of the thermoplastic polyester resin constituent of this invention is a gestalt with which the compound (B-2) which has two or more oxazoline radicals is blended in 0.1 - 10 weight section to the thermoplastic polyester (resin A) 100 weight section into the polymer (B-1) which has a carboxylic-acid reactivity radical, and/or a molecule, and it comes to blend a carboxylic anhydride (C) at a rate of 0.01 - 5 weight section. This gestalt Resin (A), a polymer (B-1), and/or a compound (B-2), And may be the gestalt which it comes to contain in the state of mixture, without an acid anhydride (C) reacting mutually, and You may be in the condition to which a part of each component reacted, i.e., the gestalt which mixture and a reactant coexist and it comes to contain, or each component may be the gestalt which it comes to contain as a reactant which reacted completely.

[0024] moreover -- this invention -- being another -- thermoplastic polyester -- resin -- a constituent -- a gestalt -- thermoplastic polyester -- resin -- (-- A --) -- 100 -- weight -- the section -- a carboxylic acid -- reactivity -- a radical -- having -- a polymer (B-1) -- and/or -- a molecule -- inside -- plurality -- oxazoline -- a radical -- having -- a compound (B-2) -- 0.1 - ten -- weight -- the section -- and -- a carboxylic anhydride -- (-- C --) -- 0.01 - five -- weight -- the section -- melting -- kneading -- carrying out -- becoming -- a gestalt -- it is . In this gestalt, some of resin (A), polymers (B-1) and/or compounds (B-2), and acid anhydrides [ at least ] (C) react by melting kneading, and the resin constituent pass this specific reaction gestalt is not only excellent in a mechanical property and endurance, but has especially the moldability which was fully excellent preferably. Once pelletizing melting kneading of each of this component using one shaft or a biaxial extruder, shaping may be presented with it and shaping may be immediately presented with it after melting kneading. Moreover, even if it carries out melting kneading processing of said each component at once, each component is kneaded separately, it may mix later, or each component may be added in 2 steps or more, and melting kneading may be carried out.

[0025] If there are few loadings of a polymer (B-1) and/or a compound (B-2) than the 0.1 weight section, a moldability and the heat-resistant improvement effectiveness will not be demonstrated, but if [ than 10 weight sections ] more, the problem of physical properties falling will occur. The loadings of a polymer (B-1) and/or a compound (B-2) are 0.1 - 7 weight section, and are 0.2 - 5 weight section more preferably. Moreover, if there are few loadings of a carboxylic anhydride (C) than the 0.01 weight section, the improvement effectiveness in a moldability will not be demonstrated, but if [ than 5 weight sections ] more, sufficient improvement effectiveness in a moldability will not be acquired upwards, and it will have a bad influence on the physical properties of mold goods. the loadings of a carboxylic anhydride (C) -- desirable -- 0.01 - 3 weight section -- more -- desirable -- 0.05 - 3 weight section -- it is 0.1 - 2 weight section further more preferably.

[0026] Under the present circumstances, the carboxylic-acid reactivity radical in the polymer (B-1) which has a carboxylic-acid reactivity radical and/or the carboxyl group in the oxazoline radical / polyester resin in a compound (B-2) = the range of 0.1-3 (mole ratio) is desirable. Unless the physical properties of the polyester resin constituent furthermore obtained are spoiled, in this invention A raw material (A), At the time of combination of (C), (B-1) And/or (B-2), at the time of shaping Polyolefines, vinyl chloride resin, such as other additives, for example, polyethylene, polypropylene, and polybutylene, A polyvinyl acetal, polyvinyl alcohol, polystyrene, an AS resin, Other thermoplastics, such as ABS plastics, a polyamide, a polycarbonate, and thermoplastic elastomer, Bulking agents, such as a pigment, a color, a reinforcement, a calcium carbonate, and talc, a heat-resistant improver, an oxidation degradation inhibitor, a plasticizer, a weatherproof improver, lubricant, a release agent, a crystalline-nucleus agent, a crystal accelerator, a fluid amelioration agent, an antistatic agent, a stabilizer, a flame retarder, etc. may be added. although especially an addition is not limited -- desirable -- the polyester resin (A) 100 weight section -- receiving -- 0 - 50 weight section -- it is 0 - 30 weight section more preferably.

[0027] As the above-mentioned additive etc., when polyolefine is included, although those mixture etc. is mentioned to polyethylene, polypropylene, polybutylenes and those copolymers, and a list, preferably, it is polyethylene, polypropylene, those copolymers, or those mixture, and, specifically, is polypropylene still more preferably. The desirable molecular weight of the above-mentioned polyolefine is the thing of 10000-100000 within the limits still more preferably within the limits of 5000-1 million. the addition of the above-mentioned polyolefine -- per above-mentioned polyester resin 100 weight section and the above-mentioned polyolefine -- 0.05 - 10 weight section -- more -- desirable -- 0.1 - 5 weight section -- it is within the limits of 0.2 - 2 weight section still more preferably.

[0028] Moreover, a glass fiber, an aramid fiber, carbon fiber, etc. are mentioned, also especially in inside, blending strengthening fiber as a reinforcement is technique well used depending on an application, for example, it is [ a glass fiber is desirable and ] a chopped glass fiber more preferably. Although not limited especially as an addition of strengthening fiber, in the case of a glass fiber, 5 - 50 % of the weight is desirable to polyester resin, and 10 - 45% is still more desirable. Moreover, in the case of an aramid fiber and carbon fiber, 2 - 50 % of the weight is desirable, and it is still more



desirable. [ of 5 - 45 % of the weight ] Although there will be especially no limit if the die length of fiber is usually used die length, it is 0.2-4mm still more preferably 0.1-5mm preferably.

[0029] Especially as the combination approaches, such as other additives, it is not limited by the compound (B-2) which has two or more oxazoline radicals, a carboxylic anhydride (C), and the need into the polymer (B-1) which has polyester resin (A) and a carboxylic-acid reactivity radical, and/or a molecule. Since the thermoplastic polyester resin constituent of this invention comes to blend the compound (B-2) and carboxylic anhydride (C) which have two or more oxazoline radicals into the polymer (B-1) which has polyester resin (A) and a carboxylic-acid reactivity radical, and/or a molecule, it has the outstanding moldability as compared with the conventional thermoplastic polyester resin constituent. It is presumed since this serves as a polymer with which the end carboxyl group which polyester resin (A) has, end hydroxyl, the carboxylic-acid reactivity radical in a polymer (B-1), the oxazoline radical in a compound (B-2), and the acid-anhydride radical of a carboxylic anhydride (C) have the molecular structure which can contribute to the outstanding moldability, such as carrying out a certain reaction or interaction, and having for example, long-chain branching as a result. On the other hand, if a process condition was not controlled to a precision when epoxy compounds, such as bisphenol female mold glycidyl ether, etc. were used, gelation was often caused.

(Application) It is a very desirable mode to use it for the various shaping approaches as mentioned above, since the thermoplastic polyester resin constituent of this invention is excellent in the moldability, and to manufacture a Plastic solid made from thermoplastic polyester resin. That is, the manufacture approach of the thermoplastic polyester resin Plastic solid of this invention is an approach of manufacturing a Plastic solid made from thermoplastic polyester resin, and is characterized by fabricating using the thermoplastic polyester resin constituent of this invention.

[0030] As for said shaping, it is desirable that it is at least one sort chosen from extrusion molding, injection molding, blow molding, foaming, and spinning shaping. Since the thermoplastic polyester resin constituent of this invention is fully conventionally excellent in the moldability compared with elegance, the mold goods which the moldability good [ without the drawdown of resin happening especially in the case of extrusion molding and blow molding ] was shown, and uniform detailed foam was obtained on the occasion of foaming, and were excellent in mechanical physical properties and an appearance by these shaping approaches are obtained. Moreover, in spinning shaping, the thread breakage stops being able to happen easily.

[0031] Although especially the making machine used with these shaping is not limited, the usual injection molding machine, the so-called injection-compression-molding machine, a twin screw extruder, a 1 shaft screw extruder, a twin screw extruder with a vent, a 1 shaft screw extruder with a vent, etc. are used preferably, for example. In the case of extrusion molding, it can fabricate by the usual approach with the extruder usually used. That is, it is fabricated by fusing the constituent of this invention with an extruder and extruding it more nearly continuously than the die of a desired configuration by a sheet, the film, etc.

[0032] In the case of injection molding, the injection molding machine usually used is used, and it can fabricate it by the usual approach. That is, the constituent of this invention can be fused within an extruder, the constituent by which melting was carried out into metal mold from the cylinder can be injected, and the Plastic solid by which size enlargement was carried out to the desired configuration can be acquired. In the case of blow molding, the blow molding machine generally used for the blow molding of thermoplastics is used, and it should just perform it by the usual approach. namely, the thermoplastic polyester resin constituent of this invention -- an extruder etc. -- plasticizing -- this -- an annular die -- extrusion -- or it injects and annular melting or the softened intermediate-field parison is formed, on both sides of this, a gas is blown into metal mold inside, it swells, cooling solidification is carried out, and it is fabricated as a hollow object. the gas blown into the interior -- air, and nitrogen and others -- although anything may be used, air usually uses from the field of economical efficiency -- having -- the blow pressure -- 3-10kg/cm<sup>2</sup> It is desirable. Furthermore, it can also fabricate with special blow molding machines, such as a three-dimension blow molding machine. Moreover, it is also possible to make the constituent of this invention into one or more layers, and to consider as a multilayer blow



molding article combining the layer by other ingredients.

[0033] In the case of foaming, the melting mixture can be mixed with a foaming agent under high pressure, and it can fabricate by carrying out melting mixing of a constituent, a thickener, etc. of this invention which adjusted loadings within an extruder, and extruding the obtained mixture to the low-pressure areas in atmospheric air etc. When extruding press machines, such as a single screw extruder, a multi-screw extruder, and a tandem extruder, can be used and it uses these extruders as an extruder which can be used by foaming, for example, said melting mixture is extruded by the low-pressure area from a mouthpiece.

[0034] The physical foaming agent which has the property to evaporate thru/or expand with heating, as said foaming agent can be used. As an example of this foaming agent, for example Inert gas; methane, such as carbon dioxide gas and nitrogen gas, Ethane, normal butane, an isobutane, a normal pentane, an isopentane, A neopentane, normal hexane, 2-methyl pentane, 3-methyl pentane, Saturated aliphatic hydrocarbon, such as 2 and 2-dimethyl butane, 2, and 3-dimethyl butane; A methyl cyclopropane, Aromatic hydrocarbon [ , such as saturation alicycle group hydrocarbon; benzene ], such as a cyclopentane, an ethyl cyclobutane, 1 and 1, and a 2-trimethyl cyclopropane; Trichloromonofluoromethane, Fluoro carbon 21, monochlorodifluoromethane, trichlorofluoroethane, Halogenated hydrocarbon, such as dichlorotetrafluoroethane; Ketones, such as ether; acetones, such as wood ether and 2-ethoxyethanol, a methyl ethyl ketone, and an acetylacetone, etc. are mentioned, and these are independent. Or two or more sorts can be mixed and used.

[0035] In order to make it the Plastic solid acquired have desired expansion ratio, to be the 1 or more sections preferably more than the 0.5 weight sections and to make it the dimensional stability of a Plastic solid not fall to said melting mixture 100 weight section at the time of extrusion molding, below 10 weight sections of the amount of said foaming agent used are desirable to said melting mixture 100 weight section, and considering as the 7.5 weight sections is more desirable.

[0036] Moreover, in order to make air bubbles fine on the occasion of foaming, it is desirable to add a foaming nucleating additive. The AZOJI carvone amide which is the organic compound generated as a foaming nucleating additive by heating inorganic gas, such as fatty-acid metal salts, such as mineral matter, such as talc, a silica, a kaolin, clay, a calcium carbonate, and an aluminum sulfate, barium stearate, and calcium stearate, a carbon dioxide, and nitrogen, azobis isobutyl dinitrile, an AZOJI carbamic acid amide, benzenesulphonyl hydrazide, etc. are illustrated. As for a foaming nucleating additive, it is desirable to carry out 0.01-5 weight section addition to the resin constituent 100 weight section of this invention. Moreover, in case foaming is carried out, in order to improve a moldability, a well-known reaction accelerator can also be used. For example, they are the metallic compounds of I, such as a sodium carbonate, II, and an III group, organometallic compounds, such as aluminum stearate, etc. The addition is range where 0.01 - 5 weight section is desirable to the resin constituent 100 weight section of this invention.

[0037] Although the spinning process condition of a conventional method can be adopted when obtaining polyester fiber with spinning shaping, as a spinning rate, it is a part for 1500-4000m/more preferably by 1500-5000m/by 1000-6000m/. Moreover, even if the 1st heated roll once takes over and it extends between the 2nd heated roll, even if it rolls round the line of thread by which melt spinning was carried out as it is, and it rolls round after heat setting (the so-called spinning direct extension), once cooling below to the glass transition temperature of a polymer on a spinning line, you may roll round after through and heating extension in a non-contact hot tube.

[0038]

[Example] Although this invention is explained concretely below, this invention is not limited to these examples.

(Molecular weight) The number average molecular weight of a polymer was measured with gel permeation chromatography (GPC).

(Intrinsic viscosity (IV)) It measured at 25 degrees C using the phenol and the mixed solvent of 6:4 (weight ratio) of tetrachloroethane.

[0039] (Evaluation of a moldability)

Foaming nature: O Expansion ratio is 20 or more times.

\*\* expansion ratio exceeds 10 times, and they are less than 20 times.

x Expansion ratio is 10 or less times.

Blow-molding nature: O Drawdown does not occur but thick uniform mold goods are obtained.

The tear at the time of a \*\* entrainment may take place.

x The tear at the time of drawdown or an entrainment takes place.

Injection-molding nature: O Surface appearance fitness.

x There is flapping a little.

Spinning moldability: O Good [ be / no thread breakage / and ].

x The thread breakage occurs frequently.

[0040] The toluene 665 section was taught to the flask equipped with the [example 1 of reference] agitator, a reflux condenser, nitrogen installation tubing, the thermometer, and the dropping funnel, and nitrogen gas was gently heated at 90 degrees C with the sink. The mixture which consists of the styrene 512 section, the 2-isopropenyl-2-oxazoline 128 section, and the par butyl O(Nippon Oil & Fats Co., Ltd. make)25 section was dropped there over 2 hours. Furthermore, after completing a reaction for stirring continuously [ 90 degrees C / for 6 hours ], it cooled to the room temperature and the resin solution was obtained. Next, after moving the obtained resin solution to the rotary evaporator and distilling off toluene by predetermined temperature and a predetermined pressure, the residue was ground and the oxazoline radical content polymer (B-1a) was obtained. By the IR spectrum, when characteristic absorption was in 1655cm<sup>-1</sup>, it checked that an oxazoline radical existed in a polymer (B-1a).

[0041] It was 6000 when the number average molecular weight of the obtained oxazoline radical content polymer (B-1a) was measured in GPC.

[Example 2 of reference] Except having replaced said 2-isopropenyl-2-oxazoline with glycidyl methacrylate, it carried out like the example 1 of reference, and the epoxy group content polymer (B-1b) was obtained. By the IR spectrum, when characteristic absorption was in 910cm<sup>-1</sup>, it checked that an epoxy group existed in a polymer (B-1b).

[0042] It was 6000 when the number average molecular weight of the obtained epoxy group content polymer (B-1b) was measured in GPC.

examples 1-4 and [examples 1-5 of comparison] thermoplastic polyester resin PET-1 (the Kanebo make --) Trade name : Pel bed PBK-1, an oxazoline radical content polymer (B-1a), An epoxy group content polymer (B-1b), 1, 3-phenylene screw oxazoline (It may abbreviate to Ox compound hereafter), bisphenol female mold glycidyl ether (It may abbreviate to Ep compound hereafter), pyromellitic acid 2 anhydride At least one sort chosen from (abbreviating to PMDA hereafter) was supplied to the biaxial extruder by the blending ratio of coal (weight section) shown in Table 1, after carrying out melting kneading, it cooled and the resin constituent pellet was prepared by the SUTARANDO cutter. Moreover, the result of having measured IV of the pellet obtained by carrying out melting kneading was shown in Table 1.

[0043] Using the resin constituent pellet obtained in examples 1-4 and the examples 1-4 of a comparison, it is a blow molding machine (Placo Make, S-45ND), and they are the die (diameter [ of 50mm ] of dice, dice spacing of 3mm) temperature of 270 degrees C, the die temperature of 80 degrees C, and 5kg/cm<sup>2</sup> of blow pressure. The average thickness of 2.5mm and the cylindrical hollow container of 500 cc of inner capacity were fabricated, and blow molding nature was evaluated. The evaluation result was shown in Table 1.

[0044] Furthermore, in examples 3-4 and the examples 1-4 of a comparison, the obtained resin constituent pellet was introduced into the injection molding machine (the Sumitomo Heavy Industries, Ltd. make, SG25-HIPRO MI1), it fabricated at the nozzle temperature of 280 degrees C, the barrel temperature of 280 degrees C, and 70% of filling pressures, and injection-molding nature was evaluated. The evaluation result was shown in Table 1. In addition, molecular weight is less than 1000, and the bisphenol female mold glycidyl ether used in the example 5 of a comparison is manufactured without passing through the so-called polymerization reaction in a manufacture process, and does not correspond to the polymer (B-1) said to this invention.

[0045]

[Table 1]

		実施例				比較例				
		1	2	3	4	1	2	3	4	5
配 合 / 重 量 部	PET-1	100	100	100	100	100	100	100	100	100
	B-1a	1	2				1			
	B-1b			1				1		
	Ox化合物				1					
	Ep化合物									1
	PMDA	0.5	0.5	0.5	0.5				0.5	0.5
IV (dl/g)		1.0	1.3	0.88	0.92	0.65	0.75	0.69	0.70	測定 不能
フロー成形性		○	○	○	○	×	△	×	×	—
射出成形性		—	—	○	○	×	○	×	×	—

[0046] examples 5-8 and [examples 6-10 of comparison] thermoplastic polyester resin PET-1 (the Kanebo make --) Trade name : Pel bed PBK-1, an oxazoline radical content polymer (B-1a), An epoxy group content polymer (B-1b), 1, 3-phenylene screw oxazoline (It may abbreviate to Ox compound hereafter), bisphenol female mold glycidyl ether (It may abbreviate to Ep compound hereafter), pyromellitic acid 2 anhydride At least one sort chosen from (abbreviating to PMDA hereafter), And talc is mixed with a tumbler as a foaming nucleating additive by the blending ratio of coal (weight section) shown in Table 2. It supplied to the extruder hopper, melting mixing was carried out, the foaming agent (isopentane) of 4 weight sections was poured in into melting mixture from the extruder middle, from nozzle metal mold, the shape of a rod was made to carry out extrusion foaming into atmospheric air, it cooled, and foam was fabricated. The laying temperature of each part of an extruder was adjusted within the limits of feed zone:268-280 degree C, compression zone:285-290 degree C, fusion zone:274-283 degree C, head section:280-290 degree C, and metal mold:265-270 degree C. The foaming nature of the acquired Plastic solid was evaluated. The evaluation result was shown in Table 2.

[0047] In addition, molecular weight is less than 1000, and the bisphenol female mold glycidyl ether used in the example 10 of a comparison is manufactured without passing through the so-called polymerization reaction in a manufacture process, and does not correspond to the polymer (B-1) said to this invention.

[0048]

[Table 2]

		実施例				比較例				
		5	6	7	8	6	7	8	9	10
配合 ／ 重 量 部	PET-1	100	100	100	100	100	100	100	100	100
	B-1a	1	2				1			
	B-1b			1				1		
	Ox化合物				1					
	Ep化合物									1
	PMDA	0.5	0.5	0.5	0.5				0.5	0.5
	タルク イソタン	0.6 4	0.6 4	0.6 4	0.6 4	0.6 4	0.6 4	0.6 4	0.6 4	0.6 4
発泡成形性		○	○	○	○	×	△	×	×	—

[0049] Examples 9-12 and [examples 11-15 of comparison] thermoplastic polyester resin PET-2 (PET pellet collected from PET film shaping waste), An oxazoline radical content polymer (B-1a), an epoxy group content polymer (B-1b), 1, 3-phenylene screw oxazoline (it may abbreviate to Ox compound hereafter), A bisphenol female mold epoxy resin (it may abbreviate to Ep compound hereafter), At least one sort chosen from pyromellitic acid 2 anhydrides (it may abbreviate to PMDA hereafter) was supplied to the biaxial extruder with a vent by the blending ratio of coal (weight section) shown in Table 3, and was fused at the barrel temperature of 280 degrees C. Melt spinning was carried out with the conventional method using the melt after melting extrusion, and it rolled round by part for 5000m/in the nozzle temperature of 280 degrees C, and rolling-up rate. Moreover, the melt in front of spinning was taken out, the result of having measured the IV was shown in Table 3, and the evaluation result of spinning nature was also further shown in Table 3.

[0050] In addition, molecular weight is less than 1000, and the bisphenol female mold glycidyl ether used in the example 15 of a comparison is manufactured without passing through the so-called polymerization reaction in a manufacture process, and does not correspond to the polymer (B-1) said to this invention.

[0051]

[Table 3]

		実施例				比較例				
		9	10	11	12	11	12	13	14	15
配合 / 重 量 部	PET-2	100	100	100	100	100	100	100	100	100
	B-1a	1	2				1			
	B-1b			1				1		
	Ox化合物				1					
	Ep化合物									1
	PMDA	0.3	0.3	0.3	0.3				0.5	0.5
IV (dl/g)		0.60	0.65	0.58	0.60	0.50	0.50	0.48	0.51	0.53
紡糸成形性		○	○	○	○	×	×	×	×	×

[0052]

[Effect of the Invention] According to this invention, the thermoplastic polyester resin constituent which it not only excels in a mechanical property and endurance, but has the moldability which was fully excellent can be offered. Especially the thermoplastic polyester resin constituent of this invention has high molecular weight and IV, and can also give reinforcement, such as toughness. A moldability specifically good [ without the drawdown of resin happening in the case of extrusion molding or blow molding ] is shown, and uniform detailed foam is obtained in the case of foaming. Moreover, since stickiness and toughness are given to resin, it is hard to generate the tear of the mold goods in the case of blow molding etc. Moreover, in spinning shaping, the problem of the thread breakage stops being able to happen easily.

[Translation done.]